Light-Scattering Characterization of Poly(tetrafluoroethylene). 2. PTFE in Perfluorotetracosane: Molecular Weight Distribution and Solution Properties

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ABSTRACT: Poly(tetrafluoroethylene) (PTFE) can be dissolved in perfluoroalkanes. With perfluorotetracosane (n-$C_{24}F_{50}$) as the solvent, two high molecular weight fractions of PTFE were characterized by using laser light scattering at 325 °C. The weight-average molecular weight (M_w) of the lower molecular weight fraction of PTFE was determined to be $(2.6 \pm 0.4) \times 10^5$ g/mol in n-$C_{24}F_{50}$ in reasonable agreement with an earlier determination of the same PTFE polymer dissolved in oligomers of poly(chlorotrifluoroethylene) at 340 °C with $M_w = 2.8 \times 10^5 \pm 10\%$ g/mol. For the static properties, we also determined the radius of gyration (R_g) = 20 ± 5 and 59 ± 8 nm and the second virial coefficient (A_2) = $(1.9 \pm 0.4) \times 10^{-5}$ and $(1.0 \pm 0.2) \times 10^{-5}$ mol mL/g^2, for the low (2.6×10^5 g/mol) and high [$(2.1 \pm 0.3) \times 10^6$ g/mol] molecular weight PTFE polymer samples, respectively. For the dynamic properties, we determined the z-average translational diffusion coefficient extrapolated to infinite dilution $\bar{D}_0^0 = 3.66 \times 10^{-7}$ and 1.21×10^{-7} cm^2/s and the diffusion second virial coefficient $k_d = -35.2$ and -130 mL/g, for the low and high molecular weight PTFE in n-$C_{24}F_{50}$ at 325 °C, respectively. By using the scaling relation $\bar{D}_0^0 = k_D M_w^{-\alpha_D}$ with k_D ($= 3.07 \times 10^{-4}$) and α_D ($= 0.54$) values based on the two PTFE characterizations in n-$C_{24}F_{50}$ at 325 °C, we could estimate the molecular weight distribution (MWD) using the measured intensity–intensity time correlation function by Laplace inversion without an a priori assumption on the form of MWD. Comparison of PTFE chain dimension with other polymer coils in solution shows that the PTFE polymer chain has similar conformation as the alkane polymer chain.

I. Introduction

Laser light scattering (LLS) has been used successfully to characterize a range of relatively intractable polymers including an alternating copolymer of ethylene and tetrafluoroethylene (denoted as PETFE) in diisobutyl adipate at 240 °C.[1-3] In a recent communication,[4] we have finally achieved, for the first time, an absolute determination of the molecular weight of poly(tetrafluoroethylene) (denoted as PTFE), $(-CF_2CF_2)_x-$, in oligomers of poly(chlorotrifluoroethylene) at 340 °C. For the PTFE polymer sample,[4,5] we determined the weight-average molecular weight M_w ($= 2.8 \times 10^5 \pm 10\%$ g/mol), the z-average radius of gyration R_g ($= 18.0 \pm 10\%$ nm), the second virial coefficient A_2 ($= 6.5 \times 10^{-5} \pm 20\%$ mol mL/g^2), the z-average translational diffusion coefficient at infinite dilution $\bar{D}_0^0$ ($= 3.26 \times 10^{-7} \pm 2\%$ cm^2/s) and the variance $\mu_2/\bar{\Gamma}^2$ ($= 0.2 \pm 10\%$). However, there were two limitations to the use of oligomers of poly(chlorotrifluoroethylene) which boiled at ~350 °C under 1-atm pressure. First, the oligomers were assumed to act as a pseudo one-component solvent. There remained a possibility of preferential solvent/polymer interactions even though we did confirm our PTFE molecular weight determination in the mixed oligomers by getting the same M_w value using two different boiling fractions of the oligomers and therefore two different oligomer compositions. Secondly, the oligomers with boiling points in the 350 °C range could not dissolve completely higher molecular weight fractions of high molecular weight PTFE polymer samples, commercially known as "Teflon" TFE fluorocarbon resin (a registered trademark of Du Pont).

In this paper, we report our findings in characterizing two PTFE polymer samples of different molecular weight in a one-component solvent in order (1) to prove our assumption that the use of oligomers as a pseudo one-component solvent is valid and (2) to determine the scaling exponent α_D in the empirical expression $\bar{D}_0^0 = k_D M_w^{-\alpha_D}$ with k_D being a proportionality constant so that we can determine the molecular weight distribution (MWD) of PTFE by means of light scattering. It should be noted that an extension of the PTFE characterization by changing the solvent from oligomers of poly(chlorotrifluoroethylene) to a normal perfluoroalkane is not trivial, even though it has been known for some time that PTFE can be dissolved in perfluoroalkanes.[6-8] For experimental convenience, we have avoided performing the high-temperature (>300 °C) light-scattering experiments under pressure. By following the concept of like dissolved like and knowing that normal alkanes dissolve polyethylene at elevated temperatures, we consider perfluoroalkanes as possible solvents for PTFE. At a pressure of 1 atm, we need a perfluoroalkane whose boiling point is near the melting temperature (~330 °C) of PTFE, since we want to avoid possibilities of crystallite formation in polymer solution. Unfortunately, with increasing boiling point and therefore increasing molecular weight, the refractive index of the intended solvent (a perfluoroalkane) must necessarily approach that of the PTFE polymer. As long-chain perfluoroalkanes are not easily available, we have to make the best possible compromise by selecting one perfluoroalkane which has a high enough boiling point to possibly dissolve the high molecular weight PTFE at high enough temperatures (~330 °C) and yet has a refractive index sufficiently different from that of PTFE to render light-scattering measurements feasible. The selected solvent has to be synthesized and purified. With very limited availability for the solvent, the solution volume required for the light-scattering experiments needs to be minimized. We chose perfluorotetracosane (n-$C_{24}F_{50}$) as the solvent for PTFE within the narrow limits of the proposed specifications. Subsequently, our studies shall also show that among normal perfluoro-

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alkanes n-$C_{24}F_{50}$ is near the limit of our two opposing requirements and is probably the only suitable solvent for light-scattering measurements of PTFE in a single solvent solution at atmospheric pressures. n-$C_{22}F_{46}$ could most probably have too low a boiling point while n-$C_{26}F_{54}$ might have a refractive index too close to that of PTFE to render light-scattering measurements even more difficult, if not impractical. A proper choice of the solvent (n-$C_{24}F_{50}$) for a definitive light-scattering characterization of PTFE is an essential prerequisite in this study. This requirement can, of course, be relaxed for other types of physical measurements of PTFE in solution, such as determination of the intrinsic viscosity.

Precise measurements of intensity–intensity time correlation function $G^{(2)}(K,\tau)$ permit us to make a Laplace inversion in order to determine an estimate of the normalized characteristic linewidth distribution function $G(\Gamma)$ with the expressions

$$G^{(2)}(K,\tau) = A(1 + b|g^{(1)}(K,\tau)|^2) \quad (1)$$

and

$$g^{(1)}(K,\tau) = \int_0^\infty G(\Gamma)e^{-\Gamma(K)\tau}\,d\Gamma \quad (2)$$

In eq 1 and 2, A is the background, b is a coherence parameter depending on the detection optics, and $g^{(1)}(K,\tau)$ is the normalized first-order electric field correlation function at scattering vector K and delay time τ. In our previous characterization,[5] we have used a variety of techniques for the Laplace inversion, including MSVD, RILIE, and CONTIN and obtained good agreement in $G(\Gamma)$ among the different Laplace inversion techniques. The Laplace inversion should always be handled with great care because of the ill-posed nature of eq 2 in the presence of noise and with limited bandwidth. The transformation of $G^{(2)}(K,\tau)$ to the molecular weight distribution (MWD) with the aid of an empirical scaling relation $\bar{D}_0^0 = k_D M^{-\alpha_D}$ is reliable only if $G(\Gamma)$ (and therefore MWD) is not too broad and the distribution is essentially unimodal. Although methods of regularization permit us to estimate $G(\Gamma)$ from $G^{(2)}(K,\tau)$ at a fixed value of K, the inversion is unique only within delicate limits. Furthermore, as $G(\Gamma)$ is intensity weighted and the scattered intensity could be proportional to the sixth power of size in the absence of interference, light scattering is dominated by larger particles and is not sensitive to the presence of a small amount of smaller particles (or lower molecular weight fractions). Thus, a light-scattering characterization of MWD tends to emphasize high molecular weight fractions while size exclusion chromatography with a refractive index detector for concentration measurements tends to emphasize lower molecular weight fractions. Furthermore, as the dynamic range of the intensity–intensity time correlation function is finite, a broad MWD could appear narrower in a light-scattering MWD characterization. Nevertheless, within the above limitations, the Laplace inversion of intensity–intensity time correlation functions for unimodal size (and therefore molecular weight) distributions of up to moderate variance ($\mu_2/\bar{\Gamma}^2 \lesssim 0.5$) of the characteristic line width should be quite reliable, especially in terms of the ratio of M_z:M_w as deduced from MWD. The two PTFE polymer samples which we studied fall within the limits of light-scattering characterization. In sections II and III, we shall briefly outline our experimental methods and discuss the results in comparison with our previous study using oligomers of poly(chlorotrifluoroethylene) as pseudo one-component solvents and with chain extension of other polymer coils in solution. In section IV, a summary with some speculation is included.

II. Experimental Methods

The details of experimental methods have been described elsewhere.[5] We shall only present the variations from the PTFE study in oligomers of poly(chlorotrifluoroethylene).

2.1. Poly(tetrafluoroethylene) Samples. The lower molecular weight PTFE samples was "DLX-6000", as experimental grade of PTFE manufactured by E.I. du Pont de Nemours and Co., Inc. It is believed to be considerably lower in molecular weight than commercial "Teflon" fluorocarbon resins. The higher molecular weight sample was made by emulsion polymerization in an aqueous medium using ammonium perfluorooctanoate as surfactant and disuccinic acid peroxide as initiator. Hydrocarbon chain transfer agent was used to control molecular weight. This sample was identical with the sample PTFE-5 described in reference (Tuminello, W. H.; Treat, T. A.; English, A. D. *Macromolecules*, in press).

2.2. Preparation of Solvent. Early workers[6] reported that PTFE was soluble in "perfluorinated kerosene" at 300°. In a later reference,[7] this material was further described as a high boiling perfluoroalkane, "FCX-412", with an average molecular formula $C_{21}F_{44}$ and an atmospheric pressure boiling temperature of about 310 °C. More recent work[8] showed that linear perfluoroalkanes of sufficiently long chain length and high boiling temperature ($T_b \geq 300$ °C, chain length ≥ 21 C atoms) should dissolve PTFE at atmospheric pressure.

In addition to dissolving polymer at atmospheric pressure, a suitable light-scattering solvent must also be thermally stable at the measurement temperature, have a refractive index sufficiently different from the polymer to give a finite value of $(\partial n/\partial C)_{T,P}$, the refractive index increment, and, ideally, be chemically pure. Perfluorotetracosane, in its pure form, meets these criteria. The solvent used in this work was made by Dr. W. Mahler by the uncatalyzed thermal coupling of purified perfluoro(1-iodododecyl iodide) at 385 °C. The crude product was washed repeatedly with acetone to remove iodine. This raw material was purified by Dr. G. J. Sloan, first by zone refining and then by continuous sublimation. The purified solvent has a sharp DSC melting peak temperature of 188.2 °C and a heat of fusion of 35.9 J/g. The boiling temperature of this purified solvent was 330 °C. Thermal stability of the solvent was assessed by sealing the solvent in thick walled glass tubing and heating in an oven at 300 °C for 48 h. After this treatment, there was no discoloration.

2.3. Preparation of Solution. The purified n-$C_{24}F_{50}$ is easier to deal with than oligomers of poly(chlorotrifluoroethylene). There is less problem with chemical degradation due to the presence of impurities. Nevertheless, solution preparation was performed under an inert atmosphere. Dissolution did take a couple of hours. In the initial run, we had anxious moments watching the PTFE solids remaining in n-$C_{24}F_{50}$ while the mixture was being stirred at 325 °C for an hour or so. The PTFE solids should be allowed to swell in the presence of a small amount of n-$C_{24}F_{50}$ at 325 °C before dissolution.

2.4. Methods of Measurements. We used the modified high-temperature light-scattering spectrometer as described in ref 5 and followed the same procedure for intensity and line-width measurements as described in ref 2.

III. Results and Discussion

3.1. Refractive Index and Refractive Index Increment Measurements. The refractive index of n-$C_{24}F_{50}$ at 325 °C was determined by using a calibrated deformed cylindrical light scattering cell with the solution/glass/air interface at the exit window oriented away from 90° to the incident laser beam. The refractive index of the solvent (n-$C_{24}F_{50}$), n_0, and the refractive index increment, $(\partial n/\partial C)_{T,P}$, of PTFE in n-$C_{24}F_{50}$ at 325 °C and $\lambda_0 = 488$ nm were determined to be 1.361 and 1.07×10^{-2} mL g^{-1}, respectively.

3.2. Light-Scattering Intensity Measurements. In a dilute polymer solution, we have

$$HC/R_{vv}(K) \cong M_w^{-1}(1 + K^2R_g^2/3) + 2A_2C \quad (3)$$

where $R_{vv}(K)$ is the excess absolute time-averaged scattered intensity using vertically polarized incident and scattered

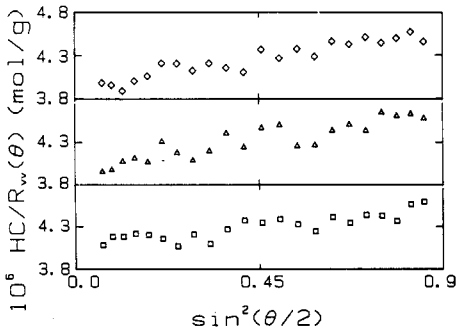

Figure 1. Plots of $HC/R_{vv}(\theta)$ vs $\sin^2(\theta/2)$ for the same PTFE polymer sample reported in ref 4 (PTFE in n-$C_{24}F_{50}$ at 325 °C). The refractive index (n_0) of the solvent (n-$C_{24}F_{50}$) was determined to be 1.361 at λ_0 = 488 nm and 325 °C. Similarly, the refractive index increment $[(\partial n/\partial C)_{T,P}]$ for PTFE in n-$C_{24}F_{50}$ was determined to be $1.07 \times 10^{-2} \simeq 1.1 \times 10^{-2}$ mL g^{-1} at the same incident wavelength and temperature. Diamonds, triangles, and squares denote $C = 2.97 \times 10^{-3}$, 4.06×10^{-3}, and 5.21×10^{-3} g/mL, respectively. $M_w \simeq (2.6 \pm 0.4) \times 10^5$ g/mol; $R_g \simeq 20 \pm 5$ nm.

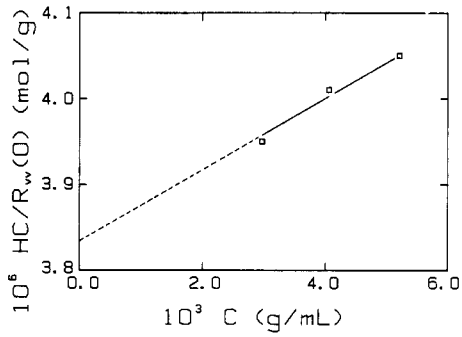

Figure 2. Plot of $\lim_{K\to 0} HC/R_{vv}(K)$ vs concentration for the same PTFE polymer samples of Figure 1. $M_w \simeq (2.6 \pm 0.4) \times 10^5$ g/mol; $A_2 \simeq (1.94 \pm 0.41) \times 10^{-5}$ mol mL/g^2.

light observed at a scattering vector K whose magnitude is $(4\pi/\lambda)\sin(\theta/2)$ with the wavelength of light in the scattering medium $\lambda = \lambda_0/n_0$ and θ being the scattering angle; H is an optical constant in units of mol cm^2 g^{-2} with $H = 4\pi^2 n_0^2 (\partial n/\partial C)_{T,P}^2/(N_A \lambda_0^4)$ and N_A being Avogadro's number; C, M_w, A_2, and R_g are, respectively, the concentration (g/mL), the weight-average molecular weight (g/mol), the second virial coefficient (mol mL/g^2), and the root-mean-square z-average radius of gyration. As the refractive index increment of PTFE in n-$C_{24}F_{50}$ at 325 °C is only of the order of 0.01 mL/g, the excess scattered intensity is very weak. Thus, instead of the usual Zimm plot, we present our scattering data in plots of $HC/R_{vv}(\theta)$ versus $\sin^2(\theta/2)$ at various fixed concentrations, as shown typically in Figure 1 for the same PTFE sample[4,5] (M_w = $2.8 \times 10^5 \pm 10\%$ g/mol) that was characterized in oligomers of poly(chlorotrifluoroethylene) (denoted as MO) at 340 °C. By extrapolation to zero concentration in a plot of $\lim_{K\to 0} HC/R_{vv}(K)$ versus concentration, as shown in Figure 2, we were able to determine the following parameters (M_w, A_2, and R_g) as listed in Table I.

By using oligomers of two boiling fractions and a one-component solvent n-$C_{24}F_{50}$, we have shown in an unambiguous way that our assumption on the use of oligomers, i.e., a pseudo multicomponent solvent is acceptable, and that we have successfully determined the molecular weight of PTFE. The negative values of A_2 for PTFE in oligomers is also reasonable since the PTFE solutions were very near the boiling point of some lower molecular weight fractions of poly(chlorotrifluoroethylene) and thus probably not far from the lower critical solution temperature. The critical effects on the determinations of M_w and R_g were, however, negligible. It is also expected that the R_g values in solvents

Table I
Static Properties (M_w, A_2, and R_g) of a PTFE Sample in Various Solvents

solv[a]	temp (°C)	M_w (10^5 g/mol)	A_2 (10^{-5} mol mL/g^2)	R_g (nm)
		Low Molecular Weight Sample		
MO-I	340	2.84 ± 10%	−6.7 ± 20%	17.8 ± 10%
MO-II	340	2.78 ± 10%	−6.2 ± 20%	18.3 ± 10%
n-$C_{24}F_{50}$	325	2.6 ± 15%	1.9 ± 21%	20 ± 25%
		High Molecular Weight Sample		
n-$C_{24}F_{50}$	325	21 ± 15%	1.0 ± 20%	59 ± 14%

[a] The symbols I and II denote the two boiling fractions of MO used to characterize the same PTFE in ref 5.

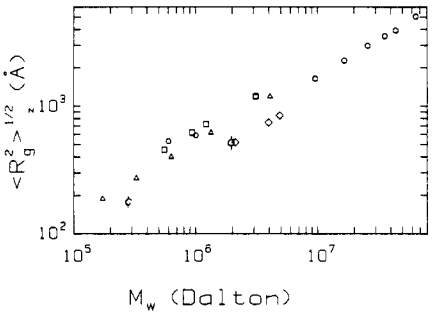

Figure 3. log–log plot of R_g vs M_w for different polymer solutions. The comparison of R_g values of PTFE with other typical polymer coils was presented in Figure 9 of ref 2. The first R_g value of PTFE in oligomers of poly(chlorotrifluoroethylene) was added in Figure 13 of ref 5. The present plot shows convincingly that the perfluoroalkane PTFE polymer chain has similar conformation as the alkane PE polymer chain: △ and ○, polystyrene in benzene (ref 9 and 10, respectively); ◇, polymethyl methacrylate in methyl methacrylate (ref 11); ○, polyethylene in 1,2,4-trichlorobenzene (ref 12); □, PETFE in diisobutyl adipate at 240 °C (ref 2); ◇, PTFE in oligomers of poly(chlorotrifluoroethylene) (ref 4) and in n-$C_{24}F_{50}$ for the low molecular weight sample and in n-$C_{24}F_{50}$ for the high molecular weight sample.

with negative A_2 values should be smaller than those in a better solvent, such as n-$C_{24}F_{50}$ where the A_2 value is positive though not very large. Figure 3 shows a log–log plot of R_g versus M_w for different polymer solutions. It is interesting to make a comparison of R_g values of PTFE and PETFE with other polymer coils. The present plot shows convincingly that the perfluoroalkane PTFE polymer chain has similar conformation as the alkane (polyethylene) polymer chain. On closer examination, we note that PTFE in its own shorter chain oligomer n-$C_{24}F_{50}$ follows the same dimension as polymethyl methacrylate (PMMA) in its own monomer methyl methacrylate (MMA).[11] Although MMA dissolves PMMA and n-$C_{24}F_{50}$ dissolves PTFE, both MMA and n-$C_{24}F_{50}$ are not really good solvents for their respective polymers, both with fairly small positive A_2 values. If we take polystyrene[9,10] (△ and ○ in Figure 3) in benzene as a reference, it appears that if PTFE were in a good solvent, its R_g values could be above those of polystyrene in benzene. We could come to the above conclusion by examining the R_g values of polyethylene (PE) in 1,2,4-trichlorobenzene[12] and PETFE in diisobutyl adipate.[2] Both PE and PETFE are in their respective fairly good solvents, though on relative terms, not as good as polystyrene (PS) in benzene. From log–log plots of R_g versus either M_w or N_w ($\equiv M_w/M_0$ with M_0 being the segment unit consisting of 4-carbon atom backbones), we see that the R_g values of PETFE are larger than those of PS or at least comparable to those of PE. Thus, the PTFE chain could be more extended, but only slightly more extended, probably because of the size of the fluorine atoms, if it were dissolved in a good solvent. Its present lower R_g values when compared with PETFE could be

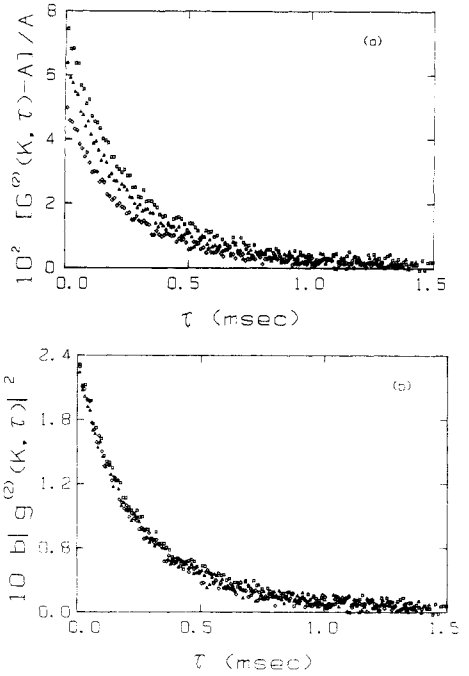

Figure 4. (a) Plots of net intensity–intensity time correlation function $[G^{(2)}(K,\tau) - A]/A$ vs delay time (τ) at different concentrations of PTFE ($M_w \simeq 2.6 \times 10^5$ g/mol) in n-$C_{24}F_{50}$ at 325 °C and $\theta = 30°$. Squares, triangles, and diamonds denote C = 5.21×10^{-3}, 4.06×10^{-3}, and 2.97×10^{-3} g/mL. (b) Plots of $b|g^{(1)}(\tau)|^2$ vs τ at the same concentrations (same symbol as Figure 4(a)).

attributed to the still fairly poor solvent quality of n-$C_{24}F_{50}$ for the longer chain perfluoroalkanes (PTFE). Our light-scattering intensity results on the conformational properties of PTFE perfluoroalkanes are in good agreement with an earlier conclusion by Stockmayer and his co-workers.[13,14] On the basis of dipole moments[13] of α,ω-dihydroperfluoroalkanes ($H(CF_2)_nH$) and α-hydro-ω-iodoperfluoroalkanes ($H(CF_2)_nI$) in benzene and carbon tetrachloride at 25 °C, as well as on light-scattering and intrinsic viscosity[14] measurements for fractions of poly(decamethylene perfluorosebacate ($[-O(CH_2)_{10}OCO(CF_2)_8CO]_x-$) in 1,1,2,2-tetrachloroethane and in chloroform at 25 °C, Stockmayer and his co-workers determined a characteristic ratio smaller than reported previously,[15] with an eventual value[14] of $C_\infty = 6.3 \pm 0.5$ while with results of R_g values for our PTFE in mixed solvents of oligomers and in n-$C_{24}F_{50}$, we can take $M_w = 2.7 \times 10^5$ g/mol, $R_g \simeq 19$ nm, and M_z:M_w:M_n = 3.8:2.1:1.0 (see next section) and estimate[16] a C_∞ value of ~7. For the higher molecular weight PTFE sample, we used the same method to obtain $M_w = 2.1 \times 10^6 \pm 15\%$ g/mol and $R_g = 59 \pm 14\%$ nm and estimated that $C_\infty \sim 8$.

We have also used the oligomers as a solvent for PETFE. By taking a calibrated PETFE polymer sample with $M_w = 9.0 \times 10^5$ g/mol, $R_g = 62$ nm, and $A_2 = 1.14 \times 10^{-4}$ mol mL/g^2 in diisobutyl adipate at 240 °C, we determined, at 240 °C, $M_w = 9.3 \times 10^5$ g/mol, $R_g = 54$ nm, and $A_2 = -2.14 \times 10^{-5}$ mol mL/g^2 in the same oligomer boiling fraction which we used to characterize PTFE at 340 °C. The negative A_2 value suggests that the presence of ethylene segments has decreased the solvent quality of oligomers of poly(chlorotrifluoroethylene) (MO) for PETFE. The contracted PETFE polymer coil in MO as compared with the more expanded PETFE coil in diisobutyl adipate attests to this supposition.

3.3. Light-Scattering Line-Width Measurements. On the basis of eq 1, we can define a net intensity–intensity time correlation function $[G^{(2)}(K,t) - A]/A \equiv b^*|g^{(1)}(K,t)|^2$ which represents the unnormalized square of the field correlation function $|g^{(1)}(K,t)|$. Figure 4a shows plots of net intensity–intensity time correlation function at three fixed concentrations of PTFE in n-$C_{24}F_{50}$ at 325 °C and $\theta = 30°$. The noise suggests a slight problem with precise determinations of $G^{(2)}(K,t)$ when the refractive index increment of the polymer solution is very small, i.e., with a refractive index increment of only 0.01 mL/g, the excess intensity of light scattered by PTFE is fairly small. We have noted an effective b^* value of less than 0.08. As the spectrometer has been apertured in a compromised mode for both light-scattering intensity and line-width measurements, we had a calibrated b value of ~0.23. The difference is due to contribution of the solvent scattering following the equation

$$G^{(2)}(K,\tau) = A\left(1 + b\left|\frac{n(\text{polymer})}{n(\text{polymer}) + n(\text{solvent})}\right|^2 |g^{(1)}(K,\tau)|^2\right) \quad (4)$$

where n(polymer) is the number of photon counts scattered by polymer molecules and n(solvent) is the number of photon counts scattered by solvent molecules. If n(polymer) $\gg$ n(solvent), the effective b^* ($\equiv b|n(\text{polymer})/[n(\text{polymer}) + n(\text{solvent})]|^2$) will be equal to real b. We shall try to take advantage of the net intensity–intensity time correlation functions measured at different concentrations by seeking a scheme to sum up the measurements so as to improve the signal-to-noise ratio of our measurements in our data analysis. In order to scale the net intensity–intensity time correlation function, it is necessary to consider the K- and concentration-dependence of the characteristic line-width Γ. Figure 4b shows the net intensity–intensity time correlation function after correction by the intensity factor $n(\text{polymer})/[n(\text{polymer}) + n(\text{solvent})]$ ($\simeq n(\text{polymer})/n(\text{solution})$), i.e., plots of $b|g^{(1)}(K,\tau)|^2$ vs τ at different concentration with $b|g^{(1)}(K,\tau)|^2 = \{[G^{(2)}(K,\tau) - A]/A\}[n(\text{solution})/n(\text{polymer})]^2$. Figure 5 shows plots of $\bar{\Gamma}/K^2$ vs K^2 for PTFE in n-$C_{24}F_{50}$ at 325 °C. The data can be represented by

$$\bar{\Gamma}/K^2 = \bar{D}_0(1 + fR_g^2K^2) \quad (5)$$

with $f \simeq 0.1$. Figure 6 shows plots of $\bar{D}_0$ vs concentration with

$$\bar{D}_0 = \bar{D}_0^0(1 + k_dC) \quad (6)$$

where k_d is the diffusion second virial coefficient and $\bar{D}_0^0$ is the z-average translational diffusion coefficient extrapolated to infinite dilution. $\bar{D}_0^0 = 1.21 \times 10^{-7}$ and 3.66×10^{-7} cm^2/s for PTFE polymers with $M_w = 2.1 \times 10^6$ and 2.6×10^5 g/mol, respectively. In the linear concentration region as represented by eq 6, the concentration depen-

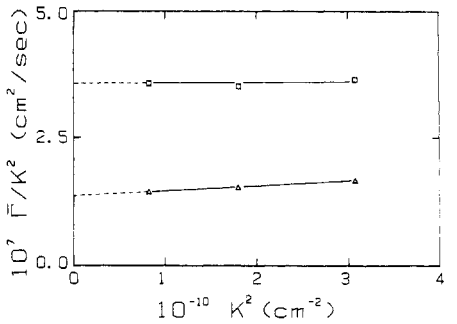

Figure 5. Plots of $\bar{\Gamma}/K^2$ vs K^2 for PTFE in n-$C_{24}F_{50}$ at 325 °C. Triangles denote $M_w = 2.1 \times 10^6$ g/mol, $C = 1.47 \times 10^{-3}$ g/mL, and $f \simeq 0.1$. Squares denote $M_w = 2.6 \times 10^5$ g/mol, $C = 2.97 \times 10^{-3}$ g/mL, and $f \simeq 0.1$. $\bar{\Gamma}/K^2$ vs K has a small slope obeying $\bar{\Gamma}/K^2 = \bar{D}_0(1 + fR_g^2K^2)$.

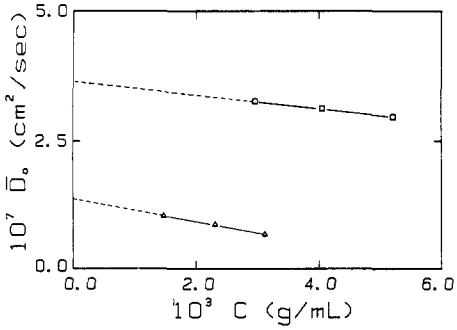

Figure 6. Plot of $\bar{D}_0$ vs C. $\bar{D}_0 = \lim_{K\to 0} \Gamma/K^2$; $\bar{D}_0^0 = \lim_{C\to 0} \bar{D}_0$; $\bar{D}_0 = \bar{D}_0^0(1 + k_d C)$. Triangles denote $M_w = 2.1 \times 10^6$ g/mol and $\bar{D}_0 = 1.21 \times 10^{-7}(1 - 1.31 \times 10^2 C)$. Squares denote $M_w = 2.6 \times 10^5$ g/mol and $\bar{D}_0 = 3.66 \times 10^{-7}(1 - 3.6 \times 10C)$. D and C expressed in cm^2/s and g/mL, respectively. Thus, $k_d = -36$ and -1.3×10^2 mL/g for the low and high molecular weight PTFE polymers, respectively.

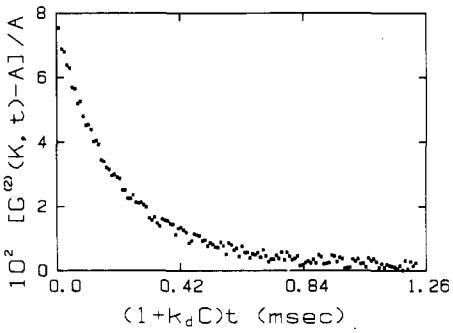

Figure 7. Plot of scaled net intensity–intensity time correlation function of PTFE in n-$C_{24}F_{50}$ at 325 °C and $\theta = 30°$. The correlation function represents sum of data points in Figure 4 scaled by the diffusion correction (due to finite concentrations) based on the virial expansion with k_d being the experimentally determined diffusion second virial coefficient.

dence of the net intensity–intensity time correlation function can be scaled, as shown in Figure 7. The increase in signal-to-noise is slight ($\sim\sqrt{3}$) as we have added only three sets of the scattering curves. Furthermore, we have taken into account the changes in the apparent b, i.e., b^*, values because the concentrations vary from 2.97×10^{-3} to 5.21×10^{-3} g/mL. If we were to use measurements at lower concentrations where solvent scattering is even more appreciable, we would have to reduce the data to $|g^{(1)}(K,\tau)|^2$ values before summation of measured data at different concentrations.

By noting the fact that over moderate widths in unimodal size distributions, different approaches[3,5] of the Laplace inversion yield essentially the same value for M_z:M_w:M_n ratios, we shall proceed with our present data analysis using only the MSVD approach.[17] Figure 8 shows plots of discrete intensity amplitudes P_i as a function of characteristic line-width Γ for the two PTFE polymer samples in n-$C_{24}F_{50}$ at 325 °C and $\theta = 30°$. The squares denote results of Laplace inversion from data denoted by diamonds in Figure 4. The relative deviations as shown in Figure 9 are appreciable though within the experimental error limits.

By using the scaling relation $\bar{D}_0^0 = k_D M_w^{-\alpha_D}$ with $k_D = 3.07 \times 10^{-4}$ and $\alpha_D = 0.54$ obtained for PTFE polymers in n-$C_{24}F_{50}$ at 325 °C, we can transform D to M and $G(D)$ to $f_w(M)$. Further, we obtained $(M_w)_{calcd} = 2.2 \times 10^5$ and 1.8×10^6 for the low and high molecular weight PTFE polymers, respectively. Both were less than the measured M_w. The errors could come from two aspects. One is from the uncertainty of the values k_D and α_D which we obtained from only two different molecular weight PTFE polymer

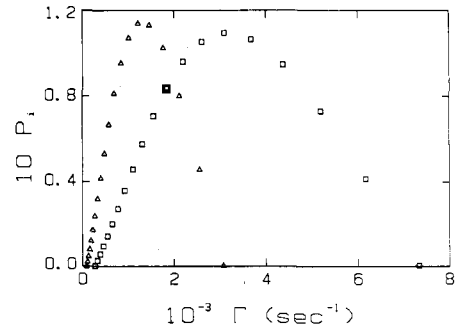

Figure 8. Plots of intensity amplitudes P_i as a function of characteristic line-width Γ for PTFE in n-$C_{24}F_{50}$ at 325 °C and $\theta = 30°$. Squares and triangles denote $M_w = 2.6 \times 10^5$ and 2.1×10^6 g/mol and $C = 2.97 \times 10^{-3}$ and 1.47×10^{-3} g/mL, respectively. The Laplace inversion was achieved by using the MSVD method[11] with $G(\Gamma) = \sum_i P_i\, \delta(\Gamma - \Gamma_i)$.

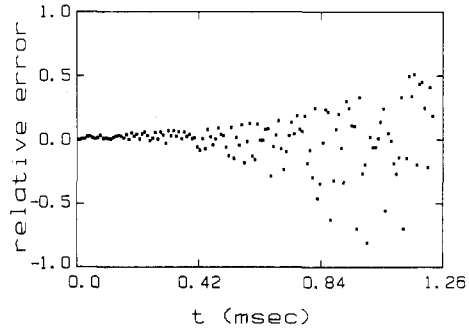

Figure 9. Relative error of the net intensity–intensity time correlation function for PTFE in n-$C_{24}F_{50}$ with $M_w = 2.6 \times 10^5$ g/mol as denoted by squares in Figure 8 and diamonds in Figure 4 at $\theta = 30°$ and 325 °C. Relative deviation = $[(b|g^{(1)}(t)|^2)_{measd} - (b|g^{(1)}(t)|^2)_{calcd}]/(b|g^{(1)}(t)|^2)_{measd}$.

samples. The other is due to the overlap of molecular weight distributions (MWD) of the two PTFE polymer samples as the molecular weight ratio was less than 10. For two fairly closely spaced polymers with an overlap in MWD, the k_D and α_D values in $\bar{D}_0^0 = k_D M_w^{-\alpha_D}$ may not be the same as those in $D_0^0 = k_D M^{-\alpha_D}$, i.e. we cannot simply use $\bar{D}_0^0$ and M_w instead of D_0^0 and M to determine k_D and α_D. In order to determine the correct k_D and α_D values, we applied the following principles. By letting $\theta \to 0$ and $C \to 0$, we have

$$\int_0^\infty G(D_0^0)\, dD_0^0 = \gamma \int_0^\infty F_z(M)\, dM \tag{7}$$

where γ is a normalization constant and $F_z(M) = MF_w(M)$. By assuming $D_0^0 = k_D M^{-\alpha_D}$, we can obtain

$$\int_\infty^0 -G(D_0^0)\alpha_D D_0^0\, d[\ln(M)] = \gamma \int_0^\infty F_z(M) M\, d[\ln(M)] \tag{8}$$

from eq 7. It can be seen from eq 8 that

$$F_z(M) = \frac{\gamma G(D_0^0)\alpha_D D_0^0}{M} \tag{9}$$

In eq 9, we have taken the integrands as one way to represent the same polymer distribution. From the definition of M_w, we have

$$M_w = \frac{\int F_w(M) M\, dM}{\int F_w(M)\, dM} \tag{10}$$

So, it is easy to rewrite eq 10 as

$$M_w = \frac{\int F_z(M)\, dM}{\int [F_z(M)/M]\, dM} \tag{11}$$

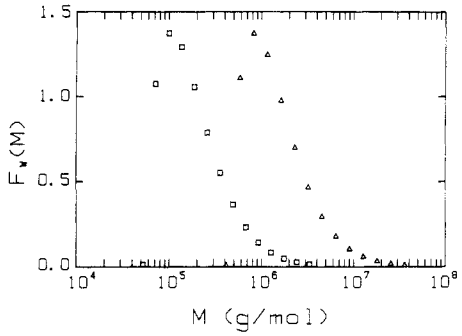

Figure 10. Molecular weight distribution of the two PTFE polymer samples in n-$C_{24}F_{50}$ at 325 °C and θ = 30°. We used the empirical relation $D_0^0 = 3.99 \times 10^{-4} M^{-0.55}$ with D_0^0 and M expressed in cm²/s and g/mol, respectively. Squares denote PTFE with $M_w = 2.6 \times 10^5$ g/mol and M_z:M_w:M_n = 3.8:2.1:1.0. Triangles denote PTFE with $M_w = 2.1 \times 10^6$ g/mol and M_z:M_w:M_n = 4.4:2.3:1.0.

By combining eq 11, eq 9, and $D_0^0 = k_D M^{-\alpha_D}$, we finally obtain

$$M_w = \frac{k_D^{1/\alpha_D} \int G(D_0^0)\, dD_0^0}{\int G(D_0^0) D_0^{01/\alpha_D}\, dD_0^0} \tag{12}$$

For the two PTFE polymer samples of different molecular weight and distribution, we have two $G(D_0^0)$, denoted as $G_1(D_0^0)$ and $G_2(D_0^0)$. From them, we could calculate two $(M_w)_{calcd}$, denoted as $(M_{w,1})_{calcd}$ and $(M_{w,2})_{calcd}$. The ratio of $(M_{w,1})_{calcd}$ and $(M_{w,2})_{calcd}$ is

$$\frac{(M_{w,1})_{calcd}}{(M_{w,2})_{calcd}} = \frac{\left[\int G_1(D_0^0)\, dD_0^0\right]\left[\int G_2(D_0^0) D_0^{01/\alpha_D}\, dD_0^0\right]}{\left[\int G_2(D_0^0)\, dD_0^0\right]\left[\int G_1(D_0^0) D_0^{01/\alpha_D}\, dD_0^0\right]} \tag{13}$$

The two calculated $(M_w)_{calcd}$ values have to equal the two measured M_w values. It means that we already know the value of the left side of eq 13. So, we can vary the value of α_D and calculate the right side of eq 13 until the left side is equal to the right side. In this way, we could find the correct α_D value. After having obtained α_D, we could easily get the k_D value by using eq 12. We applied the above method to obtain $\alpha_D = 0.55$ and $k_D = 3.99 \times 10^{-4}$ in $D_0^0 = k_D M^{-\alpha_D}$ for PTFE in n-$C_{24}F_{50}$ at 325 °C. Then, we made the transform to get $F_w(M)$ for both the low and high molecular weight PTFE polymer samples, which are shown in Figure 10.

In Figure 10, we already took out the very high molecular weight tails on the distribution curves. The contributions of those points to the cumulative molecular weight distributions are not more than 1% as shown clearly in Figure 11. We justify our truncation of the high molecular weight tail mainly to emphasize the uncertainty of the slow decay in the intensity–intensity time correlation function for PTFE in n-$C_{24}F_{50}$. Figure 12 shows a comparison of molecular weight distribution for PTFE with $M_w = 2.6 \times 10^5$ g mol using two different solvents and measured at two different temperatures. The agreement is remarkable even though we have determined the scaling relation $D_0^0 = k_D M^{-\alpha_D}$ for PTFE in n-$C_{24}F_{50}$ experimentally and only estimated the α_D value for PTFE in oligomers of poly(chlorotrifluoroethylene) because of the experimentally determined negative A_2 value. It should be noted that the estimate for α_D in oligomers was made before we performed the experiments for PTFE in n-$C_{24}F_{50}$.

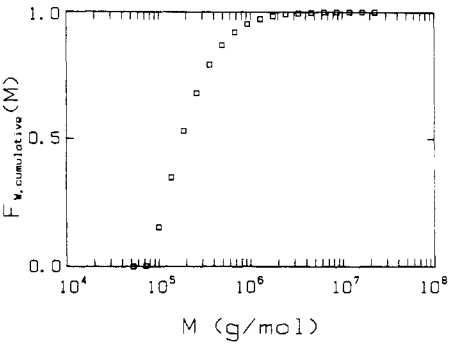

Figure 11. Cumulative molecular weight distribution of PTFE with $M_w = 2.6 \times 10^5$ g/mol. $F_{w,cumulative} = \int_0^M F_w(M)\, dM$. The high molecular weight tail is within the experimental error limits of a couple of percent. Its possible presence (or absence) cannot be established by light scattering in combination with Laplace inversion as our intensity correlation function signals were quite noisy.

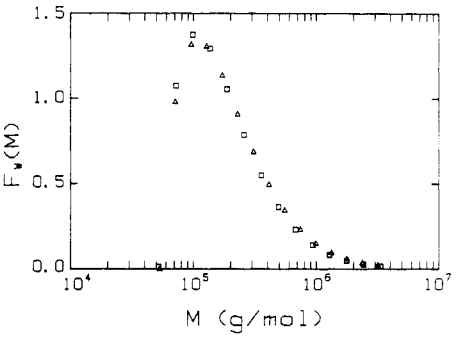

Figure 12. Comparison of molecular weight distribution for PTFE with $M_w = 2.6 \times 10^5$ g/mol using two different solvents measured at two different temperatures (symbol, solvent, temperature, empirical relation used, M_z:M_w:M_n): squares, n-$C_{24}F_{50}$, 325 °C, $D_0^0 = 3.99 \times 10^{-4} M^{-0.55}$, 3.8:2.1:1.0; triangles, oligomer, 340 °C, $D_0^0 = 1.29 \times 10^{-4} M^{-0.45}$, 3.7:2.0:1.0.

IV. Summary and Conclusions

With our success in being able to characterize PTFE solution by means of laser light scattering, it is perhaps timely to examine the possibility of using the light-scattering technique as a routine analytical tool for polymer solution characterizations. The fact that we can characterize PTFE and PETFE solutions successfully does not imply specific intrinsic difficulties associated with the operations of such a technique. Perhaps for each new type of polymer, we need to examine and to alter established procedures in any physical technique in order to optimize the parameters; and laser light-scattering is not an exception. However, as we have gained experience in characterizing a large variety of intractable polymers including "Kevlar", "Tefzel", and "Teflon" (all registered trademarks of Du Pont), the ability to use laser light scattering as a routine analytical detector, especially in conjunction with another separation technique such as size exclusion chromatography, should not be overlooked. In the following sections, we shall present the steps in our development to achieve a light-scattering characterization of Tefzel and Teflon. The outline has two purposes: (1) to provide the steps which we need to consider in using light scattering for polymer characterization purposes and (2) to include extra steps which we have taken in order to convince ourselves that we have performed the proper experiments. While we have characterized polymers which can be analyzed by other means, PTFE (Teflon) and PETFE (Tefzel) represent new characterizations which cannot yet be checked by other means at the present time. Light scattering is also a noninvasive technique. Under favorable

conditions, the entire analysis can be accomplished in minutes, if not in seconds. The steps for a light-scattering characterization are as follows: 4.1, search for a solvent, 4.2, preparation and clarification of solution, 4.3, selection of an appropriate light-scattering spectrometer, 4.4, methods of data analysis, and 4.5, precautionary measures.

4.1. Search for a Solvent. Light-scattering characterization requires that the polymer of interest is soluble in a solvent. Some polymers may aggregate in a solvent. It then becomes essential to establish experimental conditions that the polymer is dispersed without aggregation or forming a gel. For PTFE, we were able to use shorter chains (oligomers) of polyperfluoroalkanes, i.e., n-$C_{24}F_{50}$ as a solvent and oligomers of poly(chlorotrifluoroethylene) (denoted by MO) as a pseudo one-component solvent. We looked into possible preferential adsorption by a pseudo multicomponent solvent using two different boiling fractions of the same MO and obtained consistent results using both the two boiling fractions of MO and n-$C_{24}F_{50}$. The results for PTFE studies are further enforced by our studies of PETFE in a one-component solvent, diisobutyl adipate, and the same MO for PTFE. Again, consistent results in two different solvents for PETFE suggest that we have true solutions for both PTFE and PETFE. In addition, the use of oligomers could be one possible approach to other intractable polymers incapable of dissolution at accessible temperatures using conventional solvents.

4.2. Dissolution/Filtration Apparatus. Dissolution and clarification of a polymer sample in a solvent at high temperatures should include the following considerations: (i) operation under an inert atmosphere, (ii) gentle agitation of solution, (iii) transfer of solution without moving parts, since most valves would lock at high temperatures or leak without an elastomer lining, (iv) methods of cleaning the apparatus after use (in our case, by pyrolysis). We succeeded in devising such an apparatus which undoubtedly represents one of the requirements for our success. The same type of apparatus now could be used for other polymer dissolution and clarification purposes, especially in nonpolar solvents.

4.3. Selection of a Light-Scattering Spectrometer. For PTFE and PETFE characterizations, we had to construct a new high-temperature spectrometer capable of both light-scattering intensity and line-width measurements. The experiment was not trivial since in the initial design one was never sure of the minimum diameter size for the light-scattering cell suitable for the intended studies without immersing the light-scattering cell in a refractive-index matching fluid. Construction of a thermostat with an acceptable temperature gradient of $\sim$0.1 °C/cm for operation at 350 °C was another challenge as holes had to be opened for entrance and exit light beams. Our results have demonstrated that high-temperature and low-angle operations are feasible even though such instruments are not yet available commercially.

4.4. Methods of Data Analysis. Laplace inversion is an ill-conditioned problem. It is difficult for the non initiated reader to take full advantage of the many computer programs that have been developed for this purpose. The more details one wants, the more difficult and uncertain the inversion results become. This is the very nature of ill-conditioning. It is suffice to mention here that for unimodal distributions of reasonable widths many of the approaches, such as CONTIN and MSVD, are appropriate. Dynamic light-scattering does not separate particles but examines the motions of individual particles. It also emphasizes larger size particles. Thus, it would be unreasonable to ask light scattering to "see" those particles whose sizes only contribute to the scattered intensity below the limit of experimental noise. Nevertheless, we can always establish a reliable average characteristic line-width and its variance.

4.5. Precautions. The laser light-scattering method is based on dilute polymer solution behavior. Therefore, we must always consider the effects due to interparticle interactions (concentration dependence) and intraparticle interference (angular dependence), even for line-width data. The presence of long-range interactions could make extrapolation difficult because the structure factor is no longer equal to unity. Laplace inversion involving broad size distributions or bimodal size distributions (or even trimodal size distributions) are difficult though at times possible to accomplish. Again, extreme care must be exercised in using any Laplace inversion methods. In transforming size distribution to molecular weight distribution, we used an empirical relation of the form $D_0^0 = k_D M^{-a_D}$, implying that the characteristic line-width distribution deals only with translational motions of individual single particles. Thus, it is important to exclude internal motions of larger size particles in the measurement. We feel that the light-scattering procedure has been demonstrated adequately. The technique is waiting to be used as a more routine analytical tool for polymer characterization.

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References and Notes

(1) Chu, B.; Wu, C. *Macromolecules* **1986**, *19*, 1285.
(2) Chu, B.; Wu, C. *Macromolecules* **1987**, *20*, 93 and referenced therein.
(3) Wu, C.; Buck, W.; Chu, B. *Macromolecules* **1987**, *20*, 98.
(4) Chu, B.; Wu, C.; Zuo, J. *Macromolecules*, **1987**, *20*, 700.
(5) Chu, B.; Wu, C.; Buck, W. *Macromolecules* **1988**, *21*, 397.
(6) Doban, R. C.; Knight, A. C.; Peterson, J. R.; Sperati, C. A. Abstracts of Papers, 130th Meeting of Am. Chem. Soc., 1956, 98.
(7) Sperati, C. A. In *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1975; Vol. 29.
(8) Smith, P.; Gardner, K. H. *Macromolecules* **1985**, *18*, 1222.
(9) Adam, M.; Delsanti, M. *Macromolecules* **1977**, *10*, 1229.
(10) Miyaki, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978**, *11*, 1180.
(11) Chu, B.; Lee, D.-C. *Macromolecules* **1984**, *17*, 926.
(12) Chu, B.; Onclin, M.; Ford, J. R. *J. Phys. Chem.* **1984**, *88*, 6566.
(13) Matsuo, K.; Stockmayer, W. H. *J. Phys. Chem.* **1981**, *85*, 3307.
(14) Matsuo, K.; Stockmayer, W. H.; Needham, G. F. *J. Polym. Sci., Polym. Symp.* **1984**, *71*, 95.
(15) Bates, T. W.; Stockmayer, W. H. *Macromolecules* **1986**, *1*, 17.
(16) Private communication, value estimated by W. H. Stockmayer.
(17) Chu, B.; Ford, J. R.; Dhadwal, H. S. *Methods Enzymol.* **1985**, *117*, 256–297.